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Fluid-Applied Membranes

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INTRODUCTION

One of the three vital components of chemically-resistant construction is the membrane. The function of a membrane[1,6] is to protect the supporting structure (substrate) from attack by liquids (or other environment) to which it is exposed. A true membrane, as used in this paper, is defined as a total barrier to the penetration of the anticipated liquid chemical environment for the economic life of the lining. A semi-membrane is defined as one that can be penetrated, but only very slowly. The brickwork or monolithic inner liner is almost never liquid (or gas) tight, so that liquids and gases can penetrate through it, though quite slowly, and reach the membrane behind it. The purpose of the brick or monolithic liner is, therefore, to protect the membrane from extremes of heat, from mechanical abuse, and from fluid wash.[2] If the environment to which the structure is exposed attacks the structure only very slowly (as, for instance, concentrated sulfuric acid contained in a carbon steel tank), then it is not vital that the membrane provide a total barrier. A semi-membrane, one through which gas or liquid can diffuse or penetrate only very slowly, may be used in such cases to provide a construction with economical life. On the other hand, if the sulfuric acid is diluted to 30%, then the attack of the corrosive on the steel substrate becomes so rapid that any penetration[8,9] of the membrane at all will quickly damage the substrate. In such a case, a true membrane, a total barrier to penetration, is required.[3]

During the early years of this century, the most frequently used true membrane was sheet rubber.[7] Hot-applied asphalt, at least ¼" thick, was used on con-

crete floors, and in the lining of concrete vessels. In the latter case, it was reinforced with a layer of hot-applied sulfur.[4] Applications of hot asphalt to steel were largely unsuccessful due to poor adhesion to so smooth a surface and due to the sag caused by cold flow of the asphalt. Many experiments were conducted with painted or other fluid applications, and over the intervening years, a number of such materials have been identified, which if applied carefully and in sufficiently thick layers, can function effectively as true membranes. Because diffusion (permeation) rates through different materials are rarely the same, either for the attacking media or for the generic classification of the coatings, the minimum recommended thicknesses of application, in order to obtain adequate protection, vary considerably with the type of material. Obviously, there is no one material that is suitable for all exposures. The purpose of this paper is to review for the reader as many different types of fluid-applied materials as we can, together with methods of application and of test.

METHODS OF APPLICATION

The earliest methods of applying fluids as membrane applications, as we would expect, were:

(1) Melt and pour (or squeegee)–used for hot asphalt applications and some other similar materials.

(2) Brush and mop application–used for thick paint-type coatings and for hot asphalt.

(3) Air spray–used for thinner or better dispersed dispersion coatings or solution coatings.

The first two methods were preferred because they delivered the maximum material in a minimum time frame, and with minimum labor. However, it quickly became apparent that mops–though still favored today by roofers and waterproofers–do not deliver satisfactory results, for two reasons. They vary greatly in thickness due to the patterns of the mop application, and the strings from the mop are frequently found in the finished coating, which strings act as wicks and transmit through the coating the very materials the coatings are designed to act as a barrier against. Brushes are better,[3] but are used today primarily for scrubbing a primer into the surface of a substrate or for applications to rough concrete surfaces of cold-applied thick paints. Mops are completely prohibited.

Air sprays were used in the 1940s and early 1950s, in attempts to apply vinyl coatings thickly enough to act as membranes. The advent of the airless spray equipment about this time made it possible to spray a more viscous material, and so to build film thicknesses more rapidly and with fewer coats.

In the 1950s, painters started using rollers to apply paint more rapidly than by brush or spray. It is often stated that roller application provides more uniform coats and smoother finish. While rollers are excellent for smoothing a finished coat, and may be satisfactory for application on a very smooth substrate such as steel sheet, they are not as satisfactory for application to rough surfaces such as concrete where the scrubbing action of a brush may better fill the irreg-

ularities, or perhaps for porous surfaces such as some wood substrates where the impingement pressure of a spray may provide better wetting.

Through the 1930s and early 1940s, the uses of phenolic and furan mortars had become standard for "acid brick" and much experimenting was done to see if these same resins could be used as barrier coatings (membranes). Ambient temperature curing agents were used with the mortars, but these were not as effective with resins when used as coatings, due to cure shrinkage and cracking. Glass-lined vessels had been in use for some time, and the baking methods of applying glass linings were quickly adapted to phenolic resins. For a short period, furans were also applied in this manner, though such applications are no longer often noted. With the advent of fluorocarbons, this same method of heat curing of spray coatings was successfully applied to them.

In the early 1950s, the Hercules Powder Company (now Hercules, Inc.) developed a polyether resinous coating sold as Penton®, that originally showed great promise (though it has since been abandoned) which was applied in this same manner.

These additional variations of heat applications appeared about this time:

(1) Heating the target material and immersing it in a thick suspension of the coating material, a partially cured fluid resin, or even a thick solution of the resin, so the resin would migrate to the heated object and gel on the hot surface, then be further baked or ambient cured in place. This is still a favored method of applying vinyl plastisols. (Plastisols are, however, more frequently applied by airless spray.)

(2) The Schori Company pioneered hot metal spraying to apply a coating of hot metal to the surface of another metal. Though originally planned for melting or spraying metals, this same procedure has since been adapted to the application of many other coating materials, including sulfur.

(3) As a variation on these methods, the "fluidized bed" was developed. Here, a very finely ground powder of the resinous material is placed in a container and a small volume of air or neutral gas is blown into the bottom of the container to "lift" the powder and keep it floating. Into this agitated bed, the heated target is inserted so that the resin particles migrate toward and agitate against the hot surface, melt, and fuse to it. This system was successfully used with Penton® and has since been employed with other resins.

We occasionally note applications of coatings by "electrostatic deposition," an approach similar to electroplating of metals, where an electric current is passed through a suspension or solution of the coating material, and the particles of the coating material become electrically charged and are drawn and migrate to the target where they deposit and adhere themselves electrostatically.

FILLERS

To apply a fluid coating, it is obvious that the material to be used must first be fluidized. This means that it must be melted, dissolved or suspended in something, or be in a partially cured or polymerized fluid state, from which it will, after coating, solidify. Of all the items on earth, only water increases in volume when it goes from the fluid to the solid state. All dissolved materials occupy less space after they have separated out of solution or suspension. All resinous materials used today for coating, as they pass from fluid to solid condition ("cure"), will shrink in varying amounts. Therefore, in all coatings, a shrinkage stress of one type or another builds up as the coatings cure, dry or harden. Various procedures to relieve these stresses, each suited to a particular type of coating, have been developed, but some residual stress will always remain.

The more thick and viscous the coating is–the more heavily it is filled with an inert filler–the less will be the shrinkage, the less the stress and, therefore, the greater the resistance to cracking and the longer the life of the coating excluding chemical degradation. Fillers can also add strength–reinforcing–to the coating, and depending on the particle shape, may assist in making the coating a true barrier to fluid penetration (or permeation).

Among the many types of fillers in use are: powdered silica, powdered carbon or graphite, powdered resinous material, powdered barytes, nylon and other textile fibers, carbon fibers, glass fibers, and glass flakes. The powdered materials act primarily to reduce shrinkage, though they do also add some strength just as aggregate adds strength to concrete. The fibrous materials add both tensile and flexural strength to the coating. The flakes or platelets of glass, ultrathin, tiny slices of glass, do all these things, but also increase the diffusion resistance, because as the coating is applied and cured, these flakes or platelets orient themselves parallel to the surface that is being coated, and overlap each other. After the coating is cured, for any corrosive that is applied to one surface to pass through the coating to the underside, it must follow a devious path–reaching the surface of a glass flake, following the edge of the flake, and down the edge through the coating to the flake beneath, and then along that surface to the edge of that flake and down to the next flake, and so on. Thus, a true barrier may be attained if the coating is flakeglass-filled by using a lesser thickness of coating than if the coating is used alone or with another type of filler.

Some coating materials, such as epoxies, are "self-leveling." That is, they will flow to the lowest point and end up as a dead flat surface–thick on hollow spots, thinned out over peaks. If they are to be applied to vertical surfaces, either very rapid cures or the addition of some agent to make them "thixotropic" (causing them to hang in place and to prevent running) is necessary. Thixotropy is often attained by the addition of a fumed silica (for instance, Cab-O-Sil®) or by the use of a polar solvent. Plasticizers can be added to brittle or hard resins to make the coating more flexible. Bentonite clay is added to suspensions to assist in preventing settling and/or caking.

The addition of any of these filling materials, whether inert fillers, plasticizers, solvents or other modifying agents, will, of course, affect the chemical resistance of a resinous coating. The finished coating formulation does not usually have as good a resistance to certain organic materials, or to strong acids or strong alkalis, as the basic resin before it was modified. Beware of lowered chemical resistance if there is any indication that the coating materials have been modified to improve application.

Attached are two tables to help the reader understand the wide variety of possible fluid-applied membrane liners which, though not commonly thought of, might be considered for use behind brickwork. The first is a tabulation of generic types, showing the generally accepted methods of application of each. The second indicates the chemical resistances claimed for principal ones. The materials for these tables were collected from many different sources, and the author can make no claim for either completeness or accuracy. The application table may serve to guide the reader to those items which are practical for the application he had in mind, and the resistance chart to those best suited to his conditions. In all cases, the designer and user must rely on the manufacturer and applicator for specific recommendations and warranties.

Table 8-1: Application Data

Key

A - Squeegee
B - Hot Squeegee
C - Brush
D - Trowel
E - Roller
F - Air Spray
G - Airless Spray
H - Hot Spray
I - Hot Dip
J - Fluidized Bed
K - Electrostatic
L - Putty used to smooth substrate
M - Reinforcing used
N - Primer required on Steel
O - Primer optional
P - Primer required on Concrete
Q - Base coat required
R - Intermediate coat required
S - Finish coat required
T - Finish coat optional
U - Ambient cure
V - Heat cure
W - Application to concrete possible

Baked Coatings

Ceramic	F, N, Q, S, V
CTFE	F, J, K, N, S, V
E-CTFE	F, J, K, N, S, V
FEP	F, J, K, N, S, V
FEP-Amide	F, V
PFA	F, J, K, N, S, V
Phenolic	C, F, G, Q, S, V
Plastisol	F, G, I, N, S, V
PPS	F, J, K, N, S, V
PTFE	F, K, N, T, V
PTFE-Ceramic	F, N, T, V
PVDF	F, G, J, K, N, R, S, V

AMBIENT CURED COATINGS

Acrylic Latex	C, E, F, O, U, W
Asphalt Emulsion	A, C, D, E, F, G, O, P, U, W
Asphalt Hot	A, B, C, D, M, P, U, W
Asphalt Mastics	A, C, D, F, H, M, N, P, U, W
Aliphatic Polyurethane	C, E, F, G, O, P, U, W
Bitumastic	C, E, F, G, O, P, U, W
Butyl	A, C, D, E, G, N, P, U, W
Cementitious	A, C, D, U, W
Chlorinated Rubber	C, E, F, G, U, W
Coal Tar Epoxy	A, C, E, M, U, W
Epoxy	C, D, E, F, J, K, M, N, O, P, U, V, W
Epoxy Acrylic	C, E, F, G, K, O, U, W
Epoxy Asphalt	A, C, E, M, U, W
Epoxy Ester	C, E, F, G, K, O, U, W
Epoxy Phenolic	C, E, F, G, O, S, U
Epocy Phenolic Asphalt	C, E, F, G, O, U
Epoxy Polysulfide	C, D, E, N, P, U, W
Epoxy Zinc	C, F, G, S, U
Fish Oil Based	C, E, F, P, U, W
Gilsonite Asphalt	C, E, F, G, O, P, U, W
High Temp. Silicone	C, E, F, G, V
Hypalon	C, E, F, M, N, P, U, W
Inorganic Zinc Silicate	C, E, F, G, S, U
Linseed Oil	C, E, F, G, U, W
Long Oil	C, E, V, G, U, W
Neoprene	C, E, F, G, L, M, N, O, P, U, V, W
Nylon	I, J, K, V
Oleoresinous	C, E, F, G, U, W
Oil Modified Polyurethane	C, E, F, G, O, P, U, W

AMBIENT CURED COATINGS - Page 2

Organic Zinc	C, E, F, G, S, U
Oxirane Polyester	C, E, F, G, U, W
Phenolic	F, G, J, S, U
Phenolic Alkyd	C, E, F, G, U, W
Phosphate	C, E, S, U
Polyester	C, D, E, F, G, J, K, L, M, N, O, P, R, S, U, W
Polyester Epoxy	C, D, E, F, G, J, K, L, M, N, O, P, R, S, U, W
Polyurethane	C, E, F, O, P, U, W
Polyvinyl	C, E, F, G, I, J, K, L, N, O, P, U, V, W
PVA	C, E, F, G, O, T, U, W
Red Lead	C, E, F, G, S, U
Silicone Acrylic	C, E, F, G, U, W
Silicone Alkyd	C, E, F, G, U, W
Silicone Epoxy	C, E, F, G, U, W
Silicone Polyester	C, E, F, G, U, W
Soya Oil Alkyd	C, E, F, G, U, W
Styrene Butadiene	C, E, F, G, U, W
Tung Oil	C, E, F, G, U, W
Urethane	C, E, F, G, U, W
Vinyl	C, E, F, G, I, J, K, L, N, O, P, U, V, W
Vinyl Acrylic Latex	C, E, F, G, U, W
Vinyl Copolymer	C, E, F, G, U, W
Vinyl Ester	C, D, E, F, G, J, K, L, M, N, O, P, R, S, U, W
Vinyl Latex	C, E, F, U, W
Vinyl Phenolic	C, E, F, G, U, W
Viton	C, E, N, U
Wash Primer	C, E, S, U
Zinc Chromate	C, E, S, U

Table 8-2: Chemical Resistance Guide

	Furan	Epoxy	Polyester	Vinyl ester	Natural rubber	Neoprene	PVC & plastisols	Silicone	Hypalon	Urethane	Viton	Butyl	Asphalt	Nylon (Rilsan II)	Baked phenolic	Glass lined
Acetic acid - 10% and less	R	R/C	R	R	C	R	C	R	R	C	C/N	R	C	R	R	R
Acetic acid - about 10%	R	C/N	R	R	C/N	R	N	R	R	C/N	N	R/C	C	C/N	R	R
Acetone	C	N	N	N	N	C	N	R	C	N	N	R	N	R	R	R
Acetates of alcohols	R	N	N	N	N	C	N	C	N	N	N	N	N	R	R	R
Aluminum chloride and sulfate solutions	R	R	R	R	R	R	R	C	R	R	R	R	R	R	R	R
Ammonium chloride, nitrate and sulfate solutions	R	R	R	R	R	R	R	R/C	R	R	R	R	R	R	R	R
Ammonium Hydroxide	R	R	C	R	C	R	R/C	R	R	R	R	R	R	R	R	C/R
Amyl alcohol	R	N	R	R	R/C	R	R	R	R	R/C	R	R	R	-		R
Aniline	N	N	N	N	N	N	N	C	C	N	R	R	N	C/N	R	-
Barium chloride and sulfide solutions	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Barium Hydroxide	R	R	N	R	R	R	R	R	R	R	R	R	R	-	-	R
Boric acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Bromine water	N	N	R	N	N	N	C	C	R	N	R	N	N	-	C	R
Butyric acid	R	N	R	R	N	N	N	-	N	-	R		N	-	R	R
Calcium bisulfite, chloride and nitrate solutions	R	R	R	R	R	R	R	-	R	R	R	R	R	R	R	R
Calcium hydroxide to 25%	R	R	N	R	R	R	R	R	R	R	R	R	R	-	R	R
Calcium hypochlorite solution	N	R/C	R	R	N	C/N	R	C	R	N	C	R	C	R/C	R/C	R
Carbon tetrachloride	R	C	R	N	N	N	N	N	N	N	R	N	N	C/N	R	R
Chloracetic acid 10%	R	N	R	R	N	C	C	-	R	N	N	C	N	-	-	R
Chlorine dioxide	N	N	R	R	N	N	R	-	N	N	-	N	N	-	-	-
Chlorine water	N	C	R	R	C/N		R	-	-	-	R	C	C	-	C	R
Chlorobenzene	R	N	C	N	N	N	N	-	N	N	R	N	N	-	R	R
Chloroform	R	N	N	N	N	N	N	R	N	N	R	N	N	C/N	R	R
Chromic acid to 5%	N	N (C)	R	R	N	N	R	N	R	N	R	N	R	N	R/C	R/C
Cyanide plating solutions	R	R	R	R	R	R	R	R	R	R	-	R	R	-	C	R
Copper salts, solutions	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Ethyl alcohol	R	R	R	R	R	R	C/R	R	R	N	R	R	R	R/C	R	R
Ethylene dichloride	N	N	N	N	N	N	N	C	N	N	R/C	N	N	N	R	R
Ferric chloride and sulfate solutions	R	R	R	R	R	R	R	R	R	R	R	R	R	-	R	R
Hydrofluosilicic acid	R	C/N	R	R	R	R	R	N	R	-	-	C	C	-	R	N
Formaldehyde	R	R	R	R	N	R	R	C	R	N	R	R	C	R/C	R	R
Formic acid	R	C/N	R	R	N	R	C/R	C	R	N	N	R	C	N	N	R
Gasoline	R	R	R	R	N	C/N	R	C/N	C	C	R	N	N	R	R	R

CHEMICAL RESISTANCE GUIDE - Page 2.

	Furan	Epoxy	Polyester	Vinyl ester	Natural rubber	Neoprene	PVC & plastisols	Silicone	Hypalon	Urethane	Viton	Butyl	Asphalt	Nylon(Rilsan II)	Baked phenolic	Glass lined
Green liquor (paper mills)	C	C/N	C	C	R	R	R	R	C	R	-	R	-	-	N	C
Hexane	R	R	R	R	N	R	R	R	R	C	R	N	N	-	R	R
Hydrobromic acid	N	C/N	R	R	N	C	R	N	R	N	-	R	R	-	-	R
Hydrochloric acid	R	R	R	R	N	R	R	R	R	C	R	R	R	R/C	C	R
Hydrofluoric acid	R	C	R	R	N/C	R	R	C/N	R	N	R	C/R	C	-	C/N	N
Hydrogen peroxide	N/C	C	R	R	N	C/R	R	R	R	-	R	-	C	R	N	R
Jet fuel	R	R	R	R	N	C/N	R	N	C	N	R	N	N	-	-	N
Kerosene	R	R	R	R	N	C/N	R	N	C	N	R	N	N	R	-	N
Lactic acid to 20%	R	C	R	R	R	R	R	R	R	-	R	R	R	R	R	R
Magnesium salts solutions	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Maleic acid	R	N/C	R	R	N	N	R	-	N	-	-	C	R	-	-	-
Methyl alcohol	R	R	R	R	R	R	C/R	R	R	N	C	R	R	R/C	R	R
Methylene chloride	N	N	N	N	N	N	N	N	N	N	C	N	N	C	R	R
Methyl ethyl ketone	R	N	C	C	N	N	N	N	N	N	N	C	N	R	R	R
Milk	R	R	R	R	R	R	R	R	R	N	-	R	R	R	R	R
Nickel salt solutions	R	R	R	R	R	R	R	R	R	C/R	-	R	R	-	R	R
Nitric acid to 5% *	N	N	R	R	N	C/N	R	R	R	N	R	C	R	N	C	R
Nitrobenzene	R	N	N	N	N	N	N	N	N	N	C	R	N	-	R	R
Oils - Animal	R	N	R	R	N	N	C	R	C	R	-	C	-	-	-	R
Oils - Mineral	R	R	R	R	N	C/N	R	R	R	R	R	N	N	R	-	R
Oils - Vegetable	R	C	R	R	N	C	R	R	C	-	-	N	-	-	-	R
Oleic and Oxalic acids	R	N	R	R	N	C	C	N	C	C	C	N	C	R	R	R
Perchloric acid	N	N	C	C	N	N	C	N	C	N	-	C	N	-	-	R
Phenol to 5%	R	R	R	R	N	N	R	R	N	N	R	C	N	N	-	R
Phosphoric acid dilute	R	R	R	R	R	R	R	R	R	R	R	C/R	R	R	R	R
Picric acid to 10%	R	N	R	R	N	R	N	N	R	C	R	C	N	C	R	-
Potassium cyanide	R	R	R	R	R	R	R	R	R	R	-	R	R	-	C	R
Potassium hydroxide to 30%	R	R/C	N	R	R	R	R	R	R	C	R	R	R	R	N	N/R
Potassium hypochlorite to 3%	N	R/C	C	R	N	C	R	C	R	N	R	C	C	R/C	-	R
Potassium salt solutions (other)	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Sodium chromate	C	C	R	R	N	C	R	R	R	R	R	R	R	-	-	R
Sodium cyanide	R	R	C	R	R	R	R	R	R	R	-	R	R	-	C	R
Sodium hydroxide to 30%	R	R	N	R	R	R	C/R	C	R	R/C	R	R	R	R	N	C/R

CHEMICAL RESISTANCE GUIDE - Page 3.

	Furan	Epoxy	Polyester	Vinyl ester	Natural rubber	Neoprene	PVC & plastisols	Silicone	Hypalon	Urethane	Viton	Butyl	Asphalt	Nylon (Rilsan II)	Baked phenolic	Glass lined
Sodium hypochlorite to 3%	N	R/C	C	R	N	C	R	C	R	N	R	C	C	R/C	-	R
Sodium salt solutions (other)	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Stearic acid	R	N	R	R	N	C/N	C/N	R	C	R	-	C	C	R	R	C/R
Sugar (various solutions)	R	C	R	R	R	R	R	R	R	R	R	R	R		R	R
Sulfite liquor (paper mills)	R	C	R	R	R	R	R	N	C	N	-	C	-	-	R	-
Sulfur dioxide (wet and dry)	R	R	R	R	N	R	R	C/R	R	-	R	R	R	-	R	-
Sulfuric acid dilute	R	R	R	R	R	R	R	R	R	C	R	C/R	R	-	R	R
Tall oil	R	N	C	C	N	C/N	R	-	-	-	-	-	N	-	R	R
Tartaric acid	R	R	R	R	R	R	R	R	R	R	R	C/R	R	R	R	R
Toluene	R	R/C	C	C	N	N	N	N	N	N	C	N	N	R	R	R
Trichloroethylene	R	N	N	N	N	N	N	N	N	N	R	N	N	C/N	R	R
Urea solutions	R	R	R	R	R	R	R	-	-	-	-	R	R	R	R	R
White liquor (paper mills)	R	R/C	R	R	-	-	-	-	-	-	-	-	-	-	N	-
Wine	R	R/C	R	R	R	R	R	-	-	-	-	R	-	R	R	R
Xylene	R	R/C	R	R	N	N	N	C/N	N	N	R	N	N	R	R	R
Zinc salt solutions	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R

NOTE: The information summarized in this table is taken from many sources, including manufacturers' literature. The author can not guarantee it, and suggests that the user verify, with the manufacturer and by his own tests, the suitability of any coating he plans to use for exposure to his anticipated environments, prior to application.

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3. *Chemically Resistant Masonry*, Walter Lee Sheppard, Jr., cit., pp 14-16.
4. U.S. Patent No. 2,134,837, granted 1 Nov. 1938 to Claron R. Payne, on a sandwich of $^1/_8$" hot applied sulfur mortars as a reinforcing stiffener between two $^1/_8$" layers of hot-applied asphalt. This was succeeded in the 1950s by a reinforcing layer of glass fabric when that material became available.
5. There is a mass of material on sprayed rubber, but perhaps the most useful is the *Vanderbilt Rubber Handbook* published by the R.T. Vanderbilt Company of New York. The author still finds handy the 9th edition of this work, published in 1948, containing 714 pages including useful tables and index. Current edition–1978.

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